



Multi-criteria analysis of detoxification alternatives: Techno-economic and socio-environmental assessment

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ABSTRACT

The transformation of fermentable sugars provided from lignocellulosic wastes into biofuels or bioproducts is a key point at second-generation biorefineries. Spent sulfite liquor is a xylose-rich hydrolysate constituting the main residue of sulfite mills producing dissolving cellulose. Due to the presence of the inhibitors in the spent liquor, the most promising valorization options require detoxification before sugars bioconversion.

In this work, a multi criteria analysis was implemented to select techno-economic and socio-environmental feasible detoxification alternatives that can be adapted to a wide variety of fermenting scenarios. Total inhibitors removal, phenolics removal, acetic acid removal, lignosulfonates removal, total sugar losses, fixed capital invested, manufacturing costs, waste toxicity, social acceptance, and employment were chosen as the most relevant criteria. The maximum allowable concentration of undesirable inhibitors cannot be established with a general character, and thereby decision-making tools result in feasible and efficient solutions. From a technical viewpoint best solution was anionic resins with a score of 0.68; the most economical alternative was the overliming with a score of 0.76; finally, from a socio-environmental perspective, overliming reached the highest score of 0.78. In addition, three spent liquor biorefinery models were proposed. Based on the multi-criteria analysis and based on the inhibitor's concentration affecting fermentation yields and productivity, the best detoxification alternatives were (1) anionic resins for polyhydroxyalkanoate production; (2) activated carbon for ethanol biorefinery; (3) overliming for xylitol biorefinery.

1. Introduction

During the last years, many manufactures are trying to transform their processes by minimizing and re-using the obtained wastes in a circular economy thinking. In this sense, Pulp and Paper (P&P) industry is facing attractive challenges, starting from the forest, their raw material. Key factors of the transformation of this kind of industry are the spent liquors that are produced as a by-products at the end of the cooking stage [1,2]. This work is focused on the spent liquor obtained after the sulfite cooking process, that is, a chemical engineering process whose objective is the separation of the fibrous constituent of the wood (the cellulose) from the binding agent (the lignin) through the action of several chemicals (acid) in digesters at high temperatures and pressure. Once this process ends, on one hand, the pulp is obtained and must be washed, bleached, and dried; and on the other hand, the spent sulfite liquor, known as SSL is concentrated to produce energy or to be sold for further treatment [3–5].

The composition of these types of materials depends on the conditions of the process itself as well on the raw material used. The case study of this work is based on the acid sulfite process ($\text{pH} < 1.5$) and *Eucalyptus globulus* wood. Components in major proportion in this kind of by-product are lignosulfonates (42%) derived from lignin and sugars (29%) derived from hemicellulose [6,7]. Lignosulfonates can be used directly as binding agents or as chemical intermediates for the manufacture of polymers, furfuryl alcohol, vanillin, or tetrahydrofuran with high value-added applications in agriculture and fisheries, construction pharmaceuticals and cosmetics, foodstuffs, batteries, and biofuels [8]. Regarding sugars, one of the most promising valorization alternatives consists of their bioconversion into xylitol, ethanol, furfural, polyhydroxyalkanoates, succinic acid, hydrogels, or fertilizers among others [9,10].

Depolymerization and hydrolysis of hemicelluloses into fermentable sugars can release several compounds that act as microbial inhibitors hampering fermentation reactions [11]. Furthermore, the effect of the

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inhibitory compounds varies depending on their concentration, type of microorganism, and fermentation conditions used, affecting the microbial growth. Detoxification treatments have the purpose of reducing the toxic effects of inhibitors formed during biomass hydrolysis by chemical (i.e. neutralization, overliming, and ionic exchange); physical (i.e. evaporation, vacuum, membranes, extraction or adsorption); or biological (enzymatic and microbial treatments) methods [12–14]. SSL inhibitors can be divided into five groups: furan derivatives, phenolic compounds, weak acids, biomass extractives, and heavy metal ions. From these inhibitors, the most problematic are furans, phenolics, and weak acids [15,16].

The state-of-the-art of the main detoxification techniques of lignocellulosic biomass hydrolysates was reviewed by Coz et al. [11]. Previous studies in terms of detoxification of the SSL by liquid-liquid extraction [17], membranes [18,19], ionic resins, overliming, and adsorption [20], were also published by our research group and others [21,22]. In addition, some sugar valorization platforms of the SSL were also studied [6,23]. However, a deeper analysis is needed because the detoxification alternatives to be used depend not only on the inhibitors but also on the obtained products and other social and economic issues. For this reason, in this work, Multi-Criteria Analysis (MCA) decision tools were chosen to decide the best detoxification alternative based on different criteria, considering the inhibition effects and the microorganism strains over the fermentation stage, and adding the technical, economic, and socio-environmental evaluation of each detoxification option.

Decision support tools have been developed in the recent years to handle and facilitate the interpretation of data to take decisions that are more effective. Such tools can be classified in system engineering models and system assessment tools [24,25]. Among the tools developed, MCA is useful for the evaluation of different alternatives taking into account different criteria, which often conflict between them [26]. MCA has been applied in recent years in the fields of sustainable energy development issues [27], waste management [28], and nature and biodiversity conservation [29].

Just a few references were found in the literature using multi-criteria decision-making tools in a biorefinery context, and dealing with the biofuels supply chain or the lignocellulosic biomass supply [30,31]. Narani et al. [32] demonstrated the feasibility of predictive mixed effect linear models using blends of biomass for a given pretreatment. In this work, the feasibility of MCA decision support tool in determining various detoxification alternatives will be carried out in different fermenting scenarios for a given biomass hydrolysate (SSL). The chosen fermenting scenarios are focused on the production of polyhydroxyalkanoates (PHA), ethanol, and xylitol.

Is not possible to avoid degradation of inhibitory forming products during biomass pre-treatment, particularly in the case of acid pretreatment [33]. For this reason, one of the key challenges to overcome in acid sulfite P&P mills for scaling up into second-generation biorefineries relies on detoxification. Considering this step as the bottleneck, this study aims to establish which kind of detoxification is the most suitable for specific yeast and bacterial fermentation by using an MCA-based methodology. As a first step, MCA of six technical, two economic, and three socio-environmental criteria for each detoxification alternative was carried out. Secondly, some scenarios were proposed to determine the effect of the detoxification from the point of view of different stakeholders. Then, sensitivity and uncertainty analyses were performed to corroborate the robustness of the obtained solutions. Finally, and based on the MCA results, the best detoxification alternatives have been selected for each biorefinery plant (PHA, ethanol, and xylitol).

2. Methodology

2.1. Feed spent liquor characterization

Industrial SSL from calcium-based acidic sulfite-pulping of

Eucalyptus globulus supplied by Sniace SA (Torrelavega, Spain) was analyzed by previous paper [6]. To determine the homogeneity of the industrial liquor, 17 samples of pre-evaporation (weak SSL) and 17 samples of post evaporation (strong SSL) for 5 months, were analyzed.

UV-visible spectrophotometer PerkinElmer Lambda 25 was used to measure the lignosulfonates (LS) and hydroxyl phenolic groups (OH). The analysis of LS was carried out by measuring the solution absorbance at 232.5 nm.

Five types of sugars (D-xylitol, D-glucose, L-arabinose, D-mannose, and D-galactose), furfural, hydroxymethylfurfural (HMF), and acetic acid were measured by a Shimadzu HPLC using Transgenomic CARBOsep CHO-782 and SHODEX SH-1011 columns and refraction index detector [7].

2.2. Detoxification alternatives

Based on a previous review paper about detoxification processes in lignocellulosic biomass [11] and taking into account the results of characterization, the following detoxification alternatives were selected for this work: overliming (OV), anionic resin (AR), black carbon (BC), activated carbon (AC), ultrafiltration (UF), liquid-liquid extraction with Chloroform (LLC) and liquid-liquid extraction with Diethyl ether (LLD).

Optimal conditions of the selected alternatives were developed in previous research by Fernández-Rodríguez et al. [18] and Llano et al. [17,20]. The optimal conditions are specified below. OV consists of a pH adjustment of up to 10 using 2.5 M of Ca(OH)₂ at room temperature. AR experiments were conducted with Amberlite IRA-96 anion exchange resin at room temperature working at two different liquor-to-resin ratios: 6 mL of SSL per gram of wet resin (AR1) and 1.5 mL of SSL per gram of wet resin (AR2). BC experiments were carried out at 50 °C using 1:5 w/v ratio (in grams of BC per mL of SSL) and AC assays were done at 30 °C and 1:5 w/v ratio. UF was performed using 5 kDa ceramic TiO₂ membranes (IBMEM). LLD and LLC experiments were done in one single step after settling time of 30 min, 1:3 v/v (in mL of SSL per mL of solvent) using diethyl ether and chloroform organic solvents, respectively.

2.3. Economic analysis, equipment sizing, and costing

The economic analysis (see Table 1) 1 was performed following a method described by Rueda et al. [23] based on the models of Peters et al. [34] and Turton et al. [35].

All equipment was sized and priced using the same methodology as in Rueda et al. [23], based on Guthrie's method [36]. It was considered that the units are constructed of stainless steel due to the acidic pH of the SSL. Several assumptions were made for the various units. For the vessels, it was assumed that the length to diameter ratio is four. For the distillation columns, it was assumed that the tray efficiency is 80%, the tray spacing is 0.6 m, an extra feed space of 1.5 m is taken, a disengagement space of 3 m, and a skirt height of 1.5 m. The column would

Table 1
Main economic parameters used in this work.

Parameter	Calculation/Value
On-site costs	BMC
Off-site costs	0.45·On-site costs
Indirect costs	0.25·(On-site+Off-site)
Fixed Capital	On-site+Off-site+Indirect cost
FCI=(1.3·Fixed Capital)	
Operators salary	41600·(1.03) ^t (current year-2003)
Utility costs	
Cooling water	0.037 €/m ³
Low pressure steam	11 €/t
Electricity	0.0659 €/kWh
Refrigerant R407C	14000 €/t
Raw material costs	
H ₂ SO ₄	39.6 €/t
COM = 0.280·FCI+2.73·C_{OL}+1.23·(C_{UT}+C_{WT}+C_{RM})	

Table 2

Criteria for the MCA analysis of optimal detoxification of a lignocellulosic hydrolysate.

Category	Type	Criteria	Units	Abbreviation
Technical	Quantitative	C1. Total Inhibitors Removal	%	TIR
Technical	Quantitative	C2. Total Sugar Losses	%	TSL
Technical	Quantitative	C3. Acetic acid removal	%	HAcR
Technical	Quantitative	C4. Phenolics removal	%	PhR
Technical	Quantitative	C5. Lignosulfonates removal	%	LSR
Economic	Quantitative	C6. Fixed Capital Invested	€	FCI
Economic	Quantitative	C7. Manufacturing Costs	€/year	COM
Environmental	Qualitative	C8. Waste toxicity	(+++/-)	Wtox
Social	Qualitative	C9. Social acceptance	(+++/-)	Social
Social	Quantitative	C10. Employment	(employees/year)	Employ

use sieve trays and would operate at 80% of flooding capacity. Using these assumptions, complete calculations were made to size all the equipment. The mid-market dollar rate was taken as 0.83 €, on the February 21, 2021.

The Fixed Capital Invested (FCI) was estimated using the on-site costs, obtained by Guthrie's method that includes the off-site and indirect costs, the working capital, and the plant start-up cost. The Manufacturing Costs (COM) were estimated considering the operating labor cost, the utilities, waste treatment, and raw materials costs (Turton et al., 2013).

2.4. Multi-criteria analysis

The MCA analysis has been performed using the DEFINITE 3.1 software which includes a weighted summation MCA algorithm to obtain the results [28,37]. The weighted summation can be used to address problems that involve a finite and discrete set of alternatives that must be evaluated based on conflicting objectives [38]. For any given objective, one or more different attributes or criteria are used to measure the performance in relation to the objective. This methodology fits well with the problem to solve since the proposed detoxification techniques (a finite and discrete set of alternatives) present conflicting objectives (inhibitory removals versus sugar losses) and need to be analyzed from different perspectives through the developed scenarios by MCA.

Impacts of all alternative options for all criteria are presented in the impact matrix. Such criteria are usually measured on different scales and therefore cannot be compared with each other directly. The impact matrix and MCA results of the developed scenarios are shown in Tables 3 and 4, respectively.

The process to be followed to carry out weighted summation is further detailed: (1) alternatives definition that will be compared

against each other; (2) selection and definition of criteria identifying the most relevant indicators for the decision; (3) assessment of scores for each alternative by assigning values to each indicator for all the alternatives; (4) standardization of the scores to make the criteria comparable with each other; (5) weighting of criteria to assign priorities to them; (6) ranking of the alternatives. A total score for each alternative is calculated by multiplying the standardized scores with their appropriate weight, followed by summing the weighted scores of all criteria.

3. Results and discussion

3.1. Case study and selected alternatives

The spent sulfite liquor (SSL) used in this case study is composed mainly of lignosulfonates (i), sugars (ii), and inhibitors (iii). In more detail, SSL chemical composition reported in previous studies by Rueda et al. [6] and Llano et al. [39]:

- (i) Lignosulfonates (LS) (47.32 ± 4.51 g/L);
- (ii) Xylose (25.01 ± 6.23 g/L), glucose (2.35 ± 0.72 g/L), galactose (2.44 ± 0.64 g/L), mannose (1.73 ± 0.22 g/L), arabinose (1.67 ± 0.39 g/L);
- (iii) Acetic acid (6.92 ± 1.87 g/L), low molecular weight phenolics (2.27 ± 0.51 g/L), furfural (0.17 ± 0.057 g/L) and hydroxymethylfurfural (HMF) (0.03 ± 0.005 g/L).

Taking these values as a starting point, sugar fermentation is one of the most promising valorization options as per previous studies of the authors [6,20].

In this sense, based on the high xylose content of the SSL, the proposed fermenting scenarios to be assessed by MCA are the production of xylitol employing *Pichia Stipitis* [40], ethanol using two different

Table 3

Impact matrix for the multi-criteria analysis of the detoxification alternatives.

CRITERIA	ALTERNATIVES							
	OV	AR1	AR2	BC	AC	UF	LLC	LLD
C1.TIR (%)	44.9	55.1	91.8	47.6	33.6	80.6	2.4	2.9
C2.TSL (%)	11.2	15.8	63.3	42.6	56.1	60.0	0.2	1.3
C3.HAcR (%)	31.3	25.2	61.3	42.7	74.5	50.8	45.0	73.6
C4.PhR (%)	39.6	54.8	98.1	66.7	61.1	59.9	43.1	50.1
C5.LSR (%)	45.9	62.1	96.2	76.2	54.3	65.4	0.1	0.1
C6.FCI (€)	3,270,232	1,206,828	3,056,967	2,299,690	1,733,190	20,596,950	1,524,254	2,055,768
C7.COM (€/year)	113,603	5,695,709	6,235,339	2,540,033	2,382,197	421,322	1,979,869	4,723,591
C8.Wtox (+++/--)	++	-/+	-/+	-	-	-	-	-
C9.Social (+++/--)	++	++	++	-	-	+++	-	-
C10.Employ (employees/y)	5	5	5	2	2	2	4	4

Table 4
MCA results in summary of all the formulated scenarios.

Scenario	Fig.	Weights	Purpose	Best ranking position
SCE.1	Fig. 1A	50% TIR and 50% TSL	Sugar substrate inhibition and unknown fermentations	OV (0.69)
SCE.2	Fig. 1B	33.3% HAcR, PhR and LSR	All inhibitors matter	AR2 (0.97)
SCE.3	Fig. 1C	50% PhR and LSR	Bacterial fermentation	AR1 (1.00)
SCE.4	Fig. 1D	100% HAcR	Yeast fermentation	AC (1.00) and LLD (1.00)
SCE.5	Fig. 1E	20% all technical criteria	Unknown fermentation	AR2 (0.78)
SCE.6	Fig. 2A	70% TIR and TSL/30% FCI and COM	Techno-economic perspectives	OV (0.73)
SCE.7	Fig. 2B	70% FCI and COM/30% TIR and TSL		OV (0.79)
SCE.8	Fig. 2C	50% FCI and COM/50% TIR and TSL		OV (0.76)
SCE.9	Fig. 2D	50% FCI and COM/50% HAcR, PhR and LSR		AC (0.74) and OV (0.74)
SCE.10	Fig. 2E	70% HAcR, PhR and LSR/30% FCI and COM		AR2 (0.79)
SCE.11	Fig. 2F	70% FCI and COM/30% HAcR, PhR and LSR		OV (0.78)
SCE.12	Fig. 3A	20% TIR, TSL, Wtox, Social, employ	Techno-social perspectives	OV (0.74)
SCE.13	Fig. 3B	16.6% HAcR, PhR, LSR, Wtox, Social, employ		AR2 (0.82)
SCE.14	Fig. 3C	70% HAcR, PhR, LSR/30 % Wtox, Social, employ	Technical and socio-environmental perspectives	AR2 (0.88)
SCE.15	Fig. 3D	70% Wtox, Social, employ/30% HAcR, PhR, LSR		AR2 (0.76)
SCE.16	Fig. 3E	50 % Wtox/50% Social	Socio-environmental perspectives	UF (0.83)
SCE.17	Fig. 3F	30 % Wtox/30% Social/30% employ		OV (0.78)
SCE.18	Fig. 3G	30% TIR/30 % Wtox, social, employ/30% FCI and COM	Techno-economic and socio-environmental perspectives	OV (0.77)
SCE.19	Fig. 3H	10% All criteria		OV (0.73)

fermentation organisms (*Picchia Stipitis* and *Saccharomyces Cerevisiae*) [41–44], and **polyhydroxyalkanoates (PHA)** utilizing *Burkholderia Sacchari* or *Ralstonia Eutropha* [45–47]. Such bioprocesses were selected based on a literature search of the most investigated biorefinery models for the valorization of lignocellulosic biomass hydrolysates. These products can be reached by incorporating the proposed detoxification alternatives (OV, AR, BC, AC, UF, LLC, and LLD) before fermentation.

3.2. Evaluation criteria for SSL detoxification

Different categories of criteria were considered to carry out the MCA: technical (6), economic (2), and socio-environmental (3) as fully describes in Table 2. Other decision-making tools like life cycle analysis, carbon footprint, or cost-benefit analysis can also be applied in this research. Life cycle analysis or carbon footprint methods were dismissed because these tools only consider environmental aspects. The cost-benefit analysis was dismissed because only consider economic aspects. The MCA allows comparing the proposed detoxification alternatives using technical, economic, and environmental criteria simultaneously.

Apart from the technical criteria described in Table 2, others such as metal or furfurals removal, were determined in previous work [20]. Furfural concentration higher than 1.5 g/L reduced the ethanol yield by 90% and productivity by 85% [48]. Hydroxymethylfurfural (HMF) in the range of 1–5 g/L ethanol production can be reduced by 71–96% [48]. Nevertheless, contents of furfural (0.20 g/L) and HMF (0.07 g/L) found in the SSL are negligible which is why they were not considered on the criteria selected. The same occurs with levulinic and formic acids. Concentrated SSL used in OV, AR1, AR2, BC, and AC experiments, only contains 0.0031% of formic acid and 0.014% of levulinic acid. Therefore, these inhibitors were not considered in this study.

3.3. MCA results interpretation and results uncertainty

The impact matrix used in the Definite software for making the MCA is shown in Table 3. The table includes 8 quantitative criteria (5 technical and 2 economic) and 2 qualitative criteria (socio-environmental). MCA results were divided into four parts: (i) detoxification alternatives evaluated considering only technical criteria; (ii) considering techno-economic criteria; (iii) considering socio-environmental; and (iv) considering all criteria, techno-economic and socio-environmental.

A summary of MCA results as well as the contemplated scenarios are given in Table 4.

The weights distribution was assigned based on the stakeholders involved in the biorefineries supply chain. The developed scenarios represent the roles of technicians, scientists, economists, politicians, and environmental associations. An example of this can be seen in scenarios 3 and 4 (Table 4). Based on the best-ranking position reached in SCE.3, a scientist would implement anionic resins for bacterial fermentation where the worst inhibitor are phenolics [49]. Instead, based on the best ranking positions of SCE.4, a scientist would implement and activated charcoal [50,51] or liquid-liquid extraction [12] for yeast fermentation. Working with yeasts acetic acid is the worst inhibitor and this case is contemplated in SCE.4. Environmental associations probably support ultrafiltration which obtained a score of 0.78 in SCE.16 where the waste toxicity and the social acceptance were the criteria considered.

From a technical viewpoint, five scenarios were analyzed and plotted in Fig. 1. First, a compromise solution maximizing total inhibitor removal while minimizing total sugar losses was determined (Fig. 1A). These two criteria, C1.TIR and C2.TSL were assessed with a weight of 50%. In this case, the best alternative is overliming (score of 0.69) due to the lowest TSL occurred after increasing the pH of the SSL.

The second option with a similar mark of 0.68 was the treatment with anionic resin at 6 mL of SSL per gram (AR1). The second scenario (Fig. 1B) evaluates the detoxification alternatives only based on the removal of the individual inhibitors (acetic acid, phenolics, and lignosulfonates) each of them with a weight of 33.3% (HAcR; PhR; LSR). In this scenario, the best alternative with a score of 0.97 was anionic resins at 1.5 mL of SSL per gram (AR2). This scenario is useful when a new unknown bioprocess is applied because such a scenario minimizes all inhibitors that might affect the subsequent fermentation process. After AR2, the second-highest score (0.85) is the activated carbon adsorption (AC).

The third scenario analyzed comprises bacterial bioprocess for giving products like succinic acid, PHA, ABE fermentation, or bacterial cellulose. Phenolics may act on bacterial membranes, causing loss of integrity and destroying the electrochemical gradient by transporting the protons back across the mitochondrial membranes [52,53]. The third scenario gives 50% weight to phenolic compounds removal and 50% weight to lignosulfonates removal. The best alternative, as can be seen in Fig. 1C is AR2 (1.00) followed by adsorption with black carbon powder, BC (0.87).

The fourth scenario assesses the best detoxification alternative for

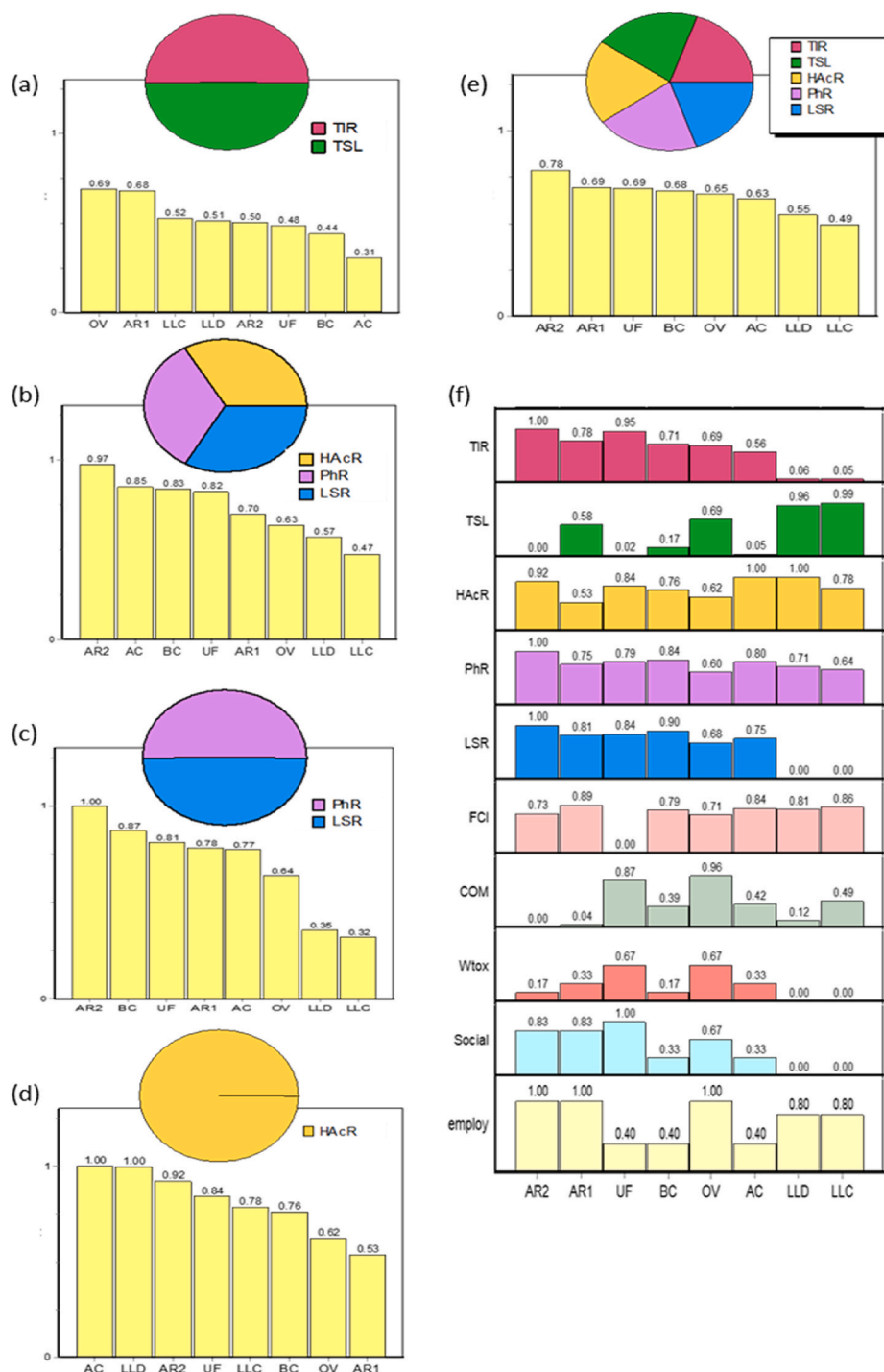


Fig. 1. Results of the rankings for the technical MCA of the detoxification alternatives.

bioprocesses working with yeast, giving products like ethanol, xylitol, lipids, carotenoids or single-cell protein [52,54,55]. The key to these bioprocesses using hydrolyzates as substrates is to adjust the pH and to get rid of the weak acids (acetic acid, levulinic acid, or formic acid). Such compounds exert a deleterious effect on yeast performance during fermentation, thereby, restraining production efficiency [56]. In this scenario, as can be seen in Fig. 1D, there are three suitable detoxification alternatives: AC with a score of 1.00; liquid-liquid extraction with diethyl ether (LLD) with a score of 1.00 and AR2 (0.92).

The last scenario of the technical MCA considers all criteria with the same weight of 20% (TIR, TSL, HAcR, PhR, LSR). This scenario, plotted in Fig. 1E and F, considers the prior uncertainty of the microorganism

nor the fermentation process. In this case, the best alternative was AR2 (0.78) followed by AR1 and UF, both with the same score (0.69).

In Fig. 2, techno-economic analysis by adding criteria C6-FCI and C7-COM to the previous set of MCA results were considered. In this case, for the different performed scenarios, weights of technical to economic were permuted from 30% to 50% and 70%. The first option (Fig. 2A) gives 70% weight to TIR, TSL, and only 30% to FCI and COM. For this reason, results are quite similar to those obtained in Fig. 1A, where the rank of detoxification alternatives is the same (only scores changed). The best option is overliming (0.69), again followed by anionic resins AR1 (0.68) and liquid-liquid extraction with chloroform, LLC (0.52).

The second option (Fig. 2B) gives 70% weight to FCI and COM whilst

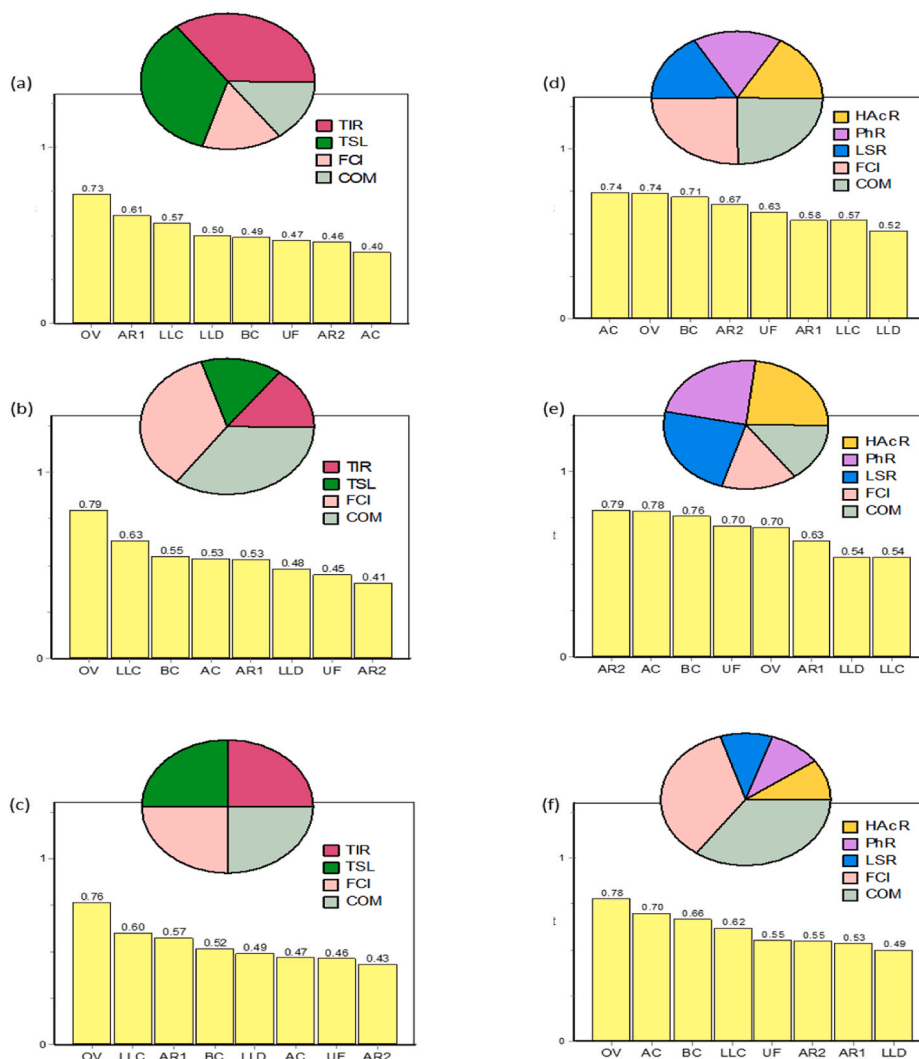


Fig. 2. Results of the rankings for the techno-economic MCA of the detoxification alternatives using the Weighted Summation methods.

the weight of TSL and TIR is 30%. Considering fixed capital costs and maintenance costs of Table 3, it seems logical that overliming (score of 0.79) is consecrated as the best option due to the low cost of the neutralizing agent and the equipment required, which is not complex. The second and third options were L-L extraction with chloroform (0.63) and black carbon adsorption (0.55), respectively. Despite AR2 is the best choice when all inhibitors should be considered from a technical viewpoint, it is the worst option from an economic point of view (score of 0.41).

The third option, presented in Fig. 2C, establishes the same weight to technical and economic criteria. The best choice would be overliming (0.76) followed by L-L extraction with chloroform (0.60), quite a similar situation to the previous study case. Apart from the economic advantages of OV and LLC due to the ease of operation and low cost of neutralizing agents and the chloroform solvent, these two detoxification alternatives present low sugar losses (11.2% for OV and only 0.2% for LLC).

The fourth, fifth, and sixth options represented in Fig. 2D, E, and 2F respectively, are analogous to the previous ones but in these cases, the chosen technical criteria were the removal of the individual inhibitors (C3.HAcR, C4.PhR, and C5.LSR). When the weights of technical and economic criteria are the same (50%), shown in Fig. 2D, the best detoxification treatments are activated carbon adsorption and overliming, with the same score (0.74). In Fig. 2C weights of economic and technical criteria are also the same but TIR and TSL instead of individual

inhibitors were chosen as technical criteria. In this case, overliming was the first choice with a similar score (0.76) but the second option was L-L extraction with chloroform (0.60). In this case, activated carbon adsorption presents better results due to the high acetic removal (74.5%) and phenolics removal (61.1%) from the SSL. In fact, the highest acetic removal was achieved with activated carbon adsorption. The fifth case, in Fig. 2E, represents scores of detoxification alternatives when the weight of individual inhibitors is 70% whereas FCI and COM weigh is 30%. In this case, the best results are anionic resins (0.79), activated carbon (0.78), and black carbon (0.76) due to its high individual inhibitor removal achieved using these techniques.

The last case represented in Fig. 2F, gives 70% weight to economic criteria and 30% to individual inhibitors removal. In this case, the most economic alternatives overliming (0.78) and activated carbon (0.70) have the highest scores within the MCA.

In Fig. 3, the last MCA tests were shown considering not only techno-economic but also socio-environmental criteria. In general, overliming and anionic resins at 1.5 mL/g (AR2) are the best alternatives among the analyzed scenarios. However, when only waste toxicity and social acceptance are considered (Fig. 3E), results change significantly with ultrafiltration (0.83), being the best alternative with a big difference concerning the rest of alternatives overliming (0.67) or resins at 6 mL/g (0.58).

Results are more balanced in Fig. 3F, when not only toxicity and social acceptance are included but also employability is added (all with

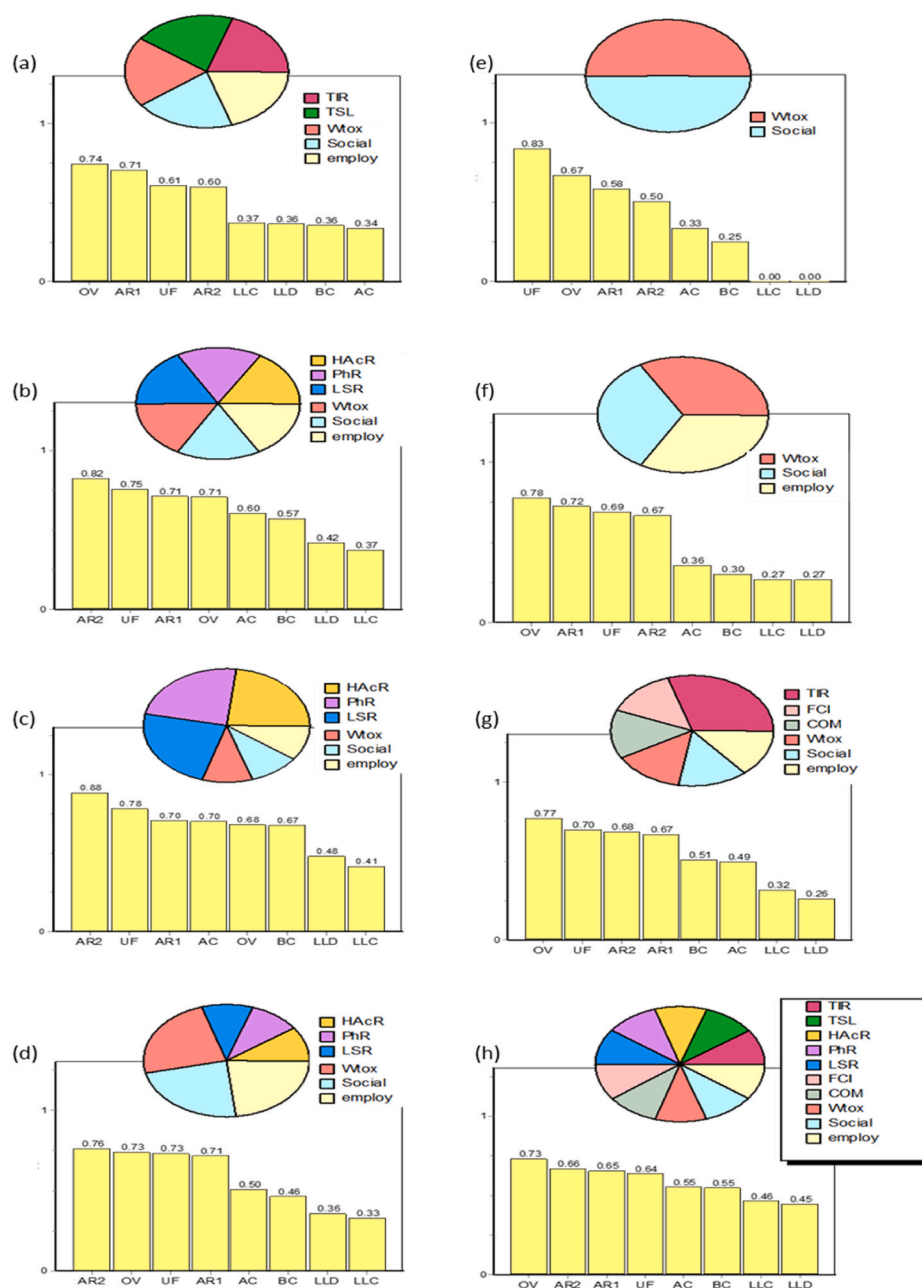


Fig. 3. Results of the rankings for the techno-economic and socio-environmental MCA of the detoxification alternatives using the Weighted Summation methods.

weights of 30%). In this case, the best results were OV (0.78) followed by AR1 (0.72), UF (0.69), and AR2 (0.67).

The last two scenarios (Fig. 3G and H) are the most complete since they consider all criteria categories. Both scenarios have the same first ranking position since overliming is enshrined as the best solution. In Fig. 3G when TIR, FCI, COM, and the socio-environmental criteria are implemented, OV (0.77) is the best option followed by UF (0.70) that reaches the second-ranking position. In Fig. 3H when the ten criteria are considered with a 10% weight, OV (0.73) is again consecrated as the best but at this time followed by AR2 (0.66).

In general terms, it can be said that, from a technical perspective, anionic resins (AR2) operating at 1.5 mL/g are at the forefront of choices. From a techno-economical perspective, overliming is the best alternative. From a socio-environmental prospect, overliming and ultrafiltration membranes are both the best options. Finally, when all criteria matter, overliming is again the best alternative.

In Fig. 4, uncertainty analysis was also carried out using Definite

software to determine the robustness of the MCA results when the impact matrix values change by 20%.

The size of the circles in Fig. 4 is proportional to the probability that each detoxification alternative occupies a certain position in the rank order. The large-sized circles on the main diagonal indicate that, despite the scores deviating from the assigned values up to 20%, the ranking of the areas hardly varied. As can be seen, overliming and anionic resins operating at 1.5 mL/g presents the best results. This analysis helps to demonstrate the robustness of the MCA results through the weighted summation methodology.

3.4. Sensitivity analysis

Sensitivity analysis assesses the influence of the weights assigned to each criterion. It is of great importance to know how the final ranking of the alternatives is sensitive to the changes of some input parameters of the decision model [37]. Sensitivity analysis after MCA has been applied

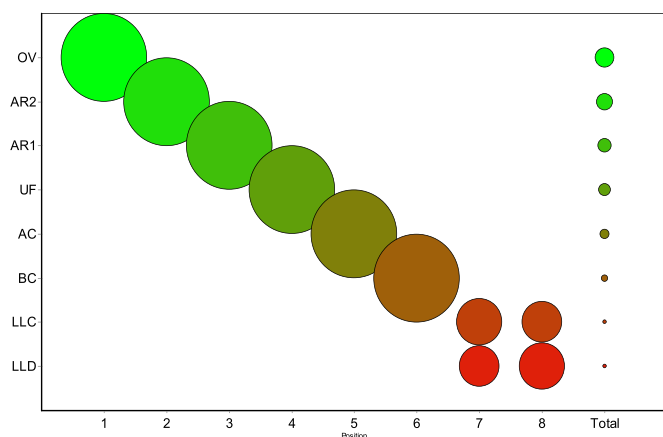


Fig. 4. Influence of criteria scores with 20% uncertainty in the ranking of the detoxification alternatives with different MCA methods.

successfully to biogas plant alternatives in the city of Reykjavik [57]. The evolution of the ranking order with the different weight distributions is represented in Fig. 5. Looking at the results in Fig. 5, in general, overliming seems to be the best detoxification alternative. This behavior occurs even at all weights of COM (Fig. 5G), waste toxicity (Fig. 5H), or employment (Fig. 5J). Recent studies reported promising results by increasing fermentability of hydrolysates using overliming. There are successful examples of overliming treatment of exhausted olive pomace [58], orange waste [59], or sugarcane bagasse [60] among others.

Nevertheless, this behavior changes when the weight of a specific criterion is higher than 25%. This happens with the total and individual inhibitors. In the case of total inhibitors removal (Fig. 5A), acetic acid removal (Fig. 5C), phenolic compounds removal (Fig. 5D), and ligno-sulfonates removal (Fig. 5E), weights upper than 25% gives the best-ranking position to AR2 alternative instead of OV. This behavior is in accordance with studies of Wang et al. [49] who compared overliming, steam stripping, liquid-liquid extraction, and ion exchange, and the highest efficiency for inhibitors removal were found using anion exchange resin D301.

In the case of TSL (Fig. 5B), when the weight is upper than 50%, LLC becomes the best detoxification technique. Studies of Roque et al. [12] resulted in low sugar consumption after liquid-liquid extraction of a xylose-rich hydrolysate. Similar behavior can be seen in Fig. 5I. When the weight of social acceptance is higher than 50%, the UF alternative has the highest score.

3.5. Application of MCA results in three biorefinery models

Based on the previous MCA results and based on the inhibitors tolerance of specific microorganisms, three biorefinery models were selected to obtain different bioproducts: PHA, ethanol, and xylitol. Thanks to the MCA results, the best detoxification technique will be chosen for ensuring an adequate fermentation for each proposed biorefinery.

PHA produced from SSL requires a detoxification step to get rid of inhibitory compounds. Several inhibitory compounds formed during hydrolysis or biomass pretreatment greatly inhibit the enzymatic hydrolysis as well as microbial fermentation [14]. The high content of phenolics, melanoidins, and sugar degradation products (furans and weak acids) stopped the cultivation of halophilic bacterium [61]. Phenolics may inhibit both microbial growth and product yield. One possible mechanism is that these compounds interfere with the cell membrane by influencing its function and changing its protein-to-lipid ratio [62]. Studies reported by Dietrich et al. [63] found a considerable range of sensitivity to microbial inhibitors in seven different bacteria. From the inhibitors contemplated (acetic, levulinic, coumaric, and

ferulic acids, syringaldehyde, HMF, and furfural), coumaryl and coniferyl-derived phenolic representatives were the most toxic on a w/v basis. Coumaric and ferulic minimum inhibitory concentration values ranged from 0.25 to 1.5 g/L strongly affect microbial fermentation as well as acetic acid concentrations ranging from 0.35 to 2.00 g/L [63]. Consequently, in a PHA SSL-based biorefinery, HAcR and PhR should be the most important technical criteria (SCE.2) together with the economic (SCE.9 and SCE.10) and the socio-environmental ones (SCE.13). Looking at the results of section 3.3, the best detoxification alternative that should be implemented before fermentation is the anionic resins at 6 mL/g (AR2).

For an ethanol biorefinery, a big bunch of experiments has been carried out regarding how different compounds inhibit the yeast/bacteria growth and those components are recognized also as formic acid, acetic acid, furfural, and HMF among others. Qiulu et al. [64] used vacuum evaporation to remove the most volatile fermentation inhibitors and increased six times the available glucose for fermentation. Ghazali and Razak [65] assessed the different detoxification techniques available for ethanol production, deciding to deeply study the effect of nanofiltration membranes over the sugar recovery from lignocellulosic hydrolysates. They conclude that the major issues found are the membrane fouling as well as the poor selectivity, which will be further studied with the influencing factors optimization. On the other hand, a study was undertaken to determine the effect of selected methods for the detoxification of an enzymatic hydrolysate from *Miscanthus giganteus* on the fermentation efficiency of saccharide derivatives [21]. They conclude that, among the detoxification procedures compared, the most beneficial effects were achieved upon the use of calcium hydroxide and activated carbon. Withing two works found in the literature, producing ethanol with the yeast *Pichia stipitis*, agree that acetic acid is responsible for the lag, the slow cell growth rate, and the ethanol production rate [66,67]. In contrast, HMF (below 10 mM) and furfural (below 5 mM) do not influence cell growth nor substrate consumption [67,68]. These results would match with those obtained by this work in scenario SCE.4 where 100% weight was assigned to the acetic removal criteria. In this case, activated carbon (1.00 score) and liquid-liquid extraction with diethyl ether (1.00 score) become the best alternatives. From these two options, if economic and environmental aspects are also included, activated carbon will be consecrated as the best detoxification alternative.

To decide the best options for xylitol production biorefinery, it is needed to check furfurals derived from pentose, as they are the major microbial growth inhibitor compounds present in chemical hydrolysates for xylitol bioconversion [69]. These compounds inhibit the growth of microbe ranging from 25 to 99% relative to the furfural concentration (0.5–2.0 g/L). Furthermore, they observed that phenolics at concentrations higher than 0.1 g/L, affect the xylose consumption, cell growth and xylitol production in *C. guilliermondii*. The effect of the acetic acid was more associated with the pKa, as its presence at low concentrations (1.0 g/L) in the fermentation medium was reported to improve the xylose-to-xylitol bioconversion [69]. A summary, different detoxification techniques were assessed and it was concluded that anion exchange resins remove high percentages of toxic compounds such as acetic acid (96%), phenolic compounds (91%), furfural (73%), HMF (70%) in addition to substantial removal of aldehydes and aliphatic acids from hydrolysates compared to anionic resins [69]. Other authors assessed the activated carbon as a detoxification technique before fermentation, increasing the xylitol production by 22.6 and 35.7% compared to those obtained using raw hydrolysate [22]. Studies of López-Linares et al. [70] assessed activated carbon and anionic resins, to check the efficiency of each one on the reduction of toxic compounds and the resulting loss of sugars and, especially, on its fermentability for xylitol production, concluding that the two methods were effective for avoiding loss of sugars, with both cases lower than 8%. However, ion-exchange resins seemed to provide slightly better protection against sugar losses than activated carbon [70]. According to SCE.1 (Fig. 1a) and SCE.6 (Fig. 2a)

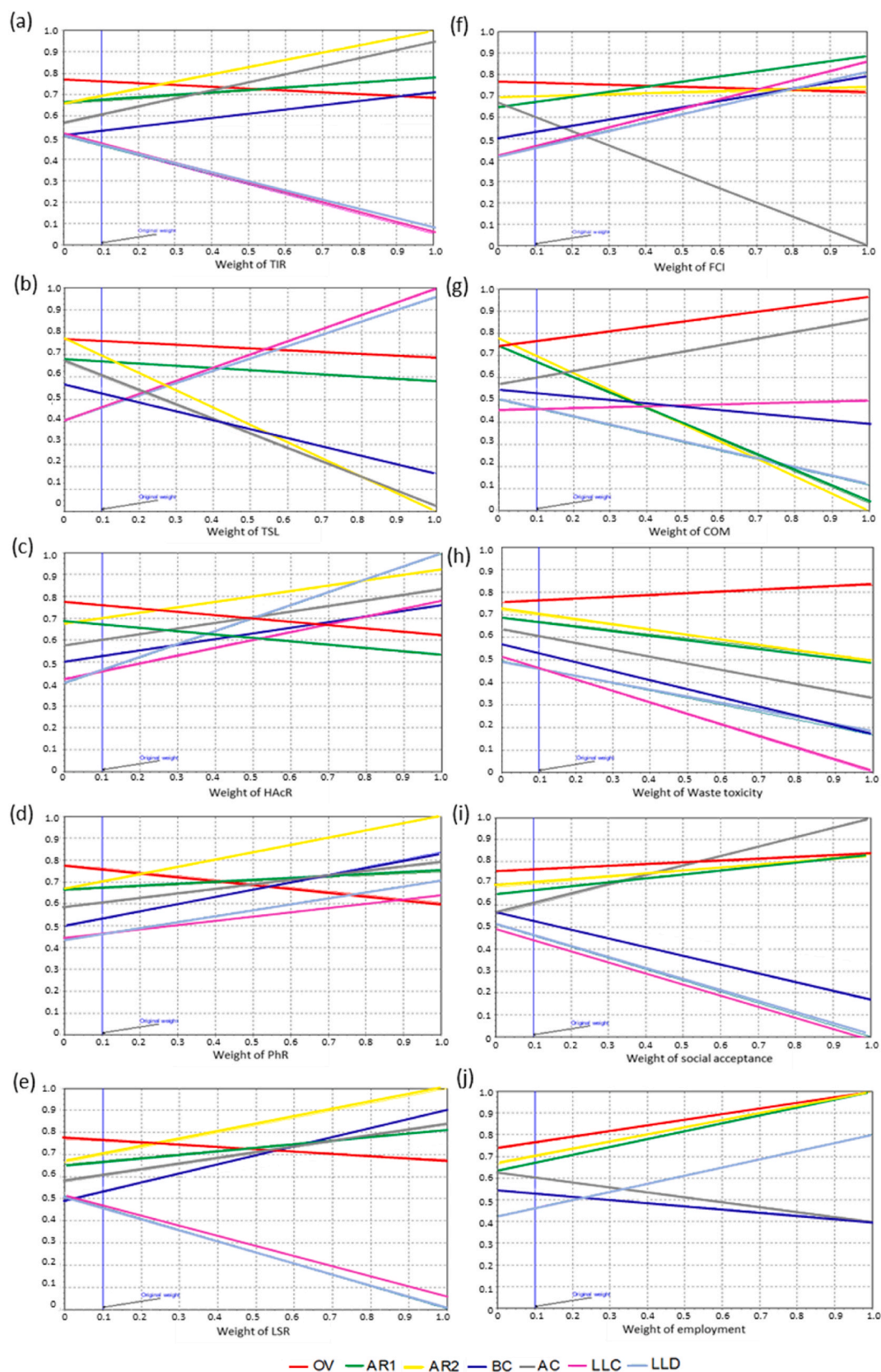


Fig. 5. Sensitivity analysis of the ranking of the detoxification alternatives to the criteria weightings with different MCA methods.

where TSL was a big impact on the final decision, overliming seems the most adequate alternative for this biorefinery proposal.

4. Conclusions

A comprehensive evaluation of detoxification alternatives of a spent sulfite liquor hydrolyzate was carried out through the application of MCA decision-making tools. The robustness of the MCA results was determined through the uncertainty analysis. A sensitivity analysis was also performed assessing the influence of the weights assigned to each criterion. In general, changes upper than 25% resulted in a change in the final ranking of the detoxification alternatives.

In summary, from a technical perspective, anionic resins are the best alternative. From a techno-economic standpoint, overliming becomes the best choice. From a socio-environmental perspective, overliming and ultrafiltration membranes are both the best options. And finally, when all criteria matter, overliming is again the best option.

Once the MCA results were checked, three bioprocesses were analyzed for obtaining PHA, ethanol, and xylitol. The best alternatives are: (1) anionic resins for PHA production; (2) activated carbon for an ethanol biorefinery; and (3) overliming for xylitol biorefinery.

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